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(54) **Free-Flowing Pearlescent Concentrate**

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European Patent Application 221,465 A
German Patent Application 3,519,080 A
German Patent Application 3,617,306 A
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Description

The present invention relates to a pearlescent concentrate in the form of a free-flowing or pumpable aqueous dispersion containing 15-40 wt% components that produce pearlescence.

An aesthetically pleasing pearlescent appearance can be imparted to aqueous preparations of surfactants and cosmetic preparations by incorporating substances which, after cooling, precipitate in the form of fine crystals with a mother of pearl appearance and remain dispersed in the preparations. Suitable pearlescing substances include, for example, the mono- and diesters of ethylene glycol, propylene glycol and oligomeric alkylene glycols of this type or glycerol with C_{16}-C_{22} fatty acids, fatty acids and monoalkanol amides of fatty acids with alkanolamines having two or three carbon atoms.

It is known that these pearlescing substances can form stable dispersions in water or in aqueous surfactant solutions, and that the concentrated pearlescent dispersions prepared in this way can be added to preparations that are to be equipped with a pearlescent appearance without heating, and thus the heating and cooling which would otherwise be necessary for incorporation are not necessary to form pearlescent crystals.

Pearlescent concentrates based on the above-mentioned pearlescing substances are known, for example, from German Patent Application 16 69 152 A, Japanese Patent 56/71021 (Chem. Abstr. 95/156360), German Patent Application 34 11 328 A and German Patent Application 35 19 081 A.

The pearlescent concentrates known from German Patent Application 16 69 152 A contain anionic surfactants to stabilize the dispersion in a liquid state. However, for many applications of such pearlescent concentrates, the presence of ionic surfactants is undesirable because they can lead to incompatibilities with ingredients of the formulation having the opposite ionicity, which can thus interfere with the stability of the dispersion.

In addition, the concentrates known from these publications also contain as part of the pearlescing substances fatty acid mono- or dialkanolamides. However, alkanolamines and their derivatives have recently been suspected of being involved in the formation of nitrosamines, and therefore it may be desirable to formulate cosmetic preparations without the use of such alkanolamines and alkanolamine derives.

Omitting the fatty acid alkanolamides from the known pearlescent concentrates, however, results in a definite reduction in the pearlescent properties. Therefore, German Patent Application 37 24 547.3 by the present applicant proposes the use of pearlescent concentrates containing as the pearlescing substance essentially linear saturated fatty acids. To obtain a satisfactory pearlescence in the end product, however, much higher concentrations of pearlescing substances are necessary.

The pearlescent concentrates known from Japanese Patent 56/71021 have the disadvantage that they are not free-flowing and they do not form stable free-flowing dispersions when diluted appropriately with water. Therefore, this makes handling and industrial processing of concentrates much more difficult.

However, there is still a high demand for pearlescent concentrates with high concentrations of pearlescing components that have the same stability, are free-flowing or pumpable and can be incorporated well into the products that are to be finished with a pearlescence, regardless of their anionic or cationic ingredients. In addition, it should also be possible to formulate the concentrates so that they are free of alkanolamides if desired and to impart to the end product the desired pearlescence even at the usual concentrates of pearlescing components in the end product.

It has now been found that all these requirements are met by a pearlescence concentrate in the form of a free-flowing aqueous dispersion which is characterized in that it contains

(A) 15-40 wt% pearlescing components
(B) 5-55 wt% nonionic ampholytic and/or zwitterionic emulsifiers and
(C) 0.1-5 wt% low molecular polyhydric alcohols.

Especially advantageous properties are shown by pearlescent concentrates containing

(A) 20-30 wt% pearlescing components
(B) 15-30 wt% nonionic, ampholytic and/or zwitterionic emulsifiers and
(C) 0.5-3 wt% low molecular polyhydric alcohols.

Pearlescing components are understood to be meltable fatty or waxy substances which crystallize out in the form of fine pearlescent bodies when their aqueous solutions or emulsions are cooled in a temperature range of approximately 30-90°C.

Preferred pearlescing components include

(A1) esters of formula (I),

$$R^1 - (OC_n H_{2n})_x - OR^2$$

where R^1 is a linear fat acyl group with 14 to 22 carbon atoms, R^2 is hydrogen or an R^1 group, n = 2 or 3 and x is a number from 1 to 4,

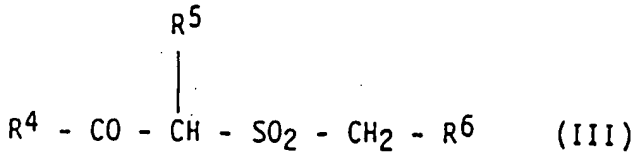
(A2) monoalkanolamides of general formula (II)

$$R^3\text{-}CO\text{-}NH\text{-}X$$

where R^3 is an alkyl group with 8 to 22 carbon atoms, in particular with 8 to 18 carbon atoms, and x is a $-CH_2-CH_2-OH$ group, a $-CH_2-CH_2-CH_2-OH$ group or a $-C(CH_3)_2-OH$ group,

(A3) linear, saturated fatty acids with 6 to 22 carbon atoms and

(A4) β-ketosulfones of general formula (III),



$$R^4 - CO - CH(R^5) - SO_2 - CH_2 - R^6 \qquad (III)$$

where R^4 is an alkyl group or an alkenyl group with 11 to 21 carbon atoms, R^5 and R^6 are hydrogen atoms or together they may form an ethylene group which forms a tetrahydrothiophene dioxide ring together with the group between R^5 and R^6.

The pearlescent concentrates according to this invention may contain only the representatives of one of these classes of compounds or they may also contain mixtures of representatives of several of these classes of compounds.

For example, the esters (A1) of general formula $R^1(OC_nH_{2n})_xOR^2$ which may be used include the mono- and diesters of ethylene glycol and propylene glycol with higher fatty acids such as palmitic acid, stearic acid or behenic acid or the diesters of diethylene glycol or triethylene glycol with such fatty acids. Mixtures of mono- and diesters of these glycols with fatty acid mixtures such as hardened tallow fatty acid or with the saturated C_{14}-C_{18} fatty acid fraction of tallow fatty acid are also suitable. The ethylene glycol mono- and/or diesters of palmitic acid and/or stearic acid are preferred.

Preferred monoalkanolamides (A2) include the monoethanolamides. These compounds may contain a uniform alkyl group. However, it is conventional to start with fatty acid mixtures from natural sources such as coconut fatty acids in preparing the alkanolamides, so that the resulting products are corresponding mixtures with regard to the alkyl groups.

Examples of linear fatty acids (A3) that may be used include palmitic acid, stearic acid, arachinoic acid or behenic acid, but technical grade fatty acid cuts consisting entirely or mainly of fatty acids with 16 to 22 carbon atoms such as palmitic acid-stearic acid fractions like those obtained from tallow fatty acid by separating the fatty acids that are liquid at +5°C or palmitic acid-stearic acid fractions such as those accessible by hardening tallow fatty acid.

In comparison with the known ethylene glycol mono- and diesters, the β-ketosulfones (A4) of general formula (III) have the advantage that the pearlescence of the preparations has a greater thermal stability, i.e., the pearlescence is preserved for several hours even when the preparations are heated to temperatures above 50°C, or in some cases even to more than 70°C. With regard to further information concerning the above-mentioned β-ketosulfones, reference is made explicitly to the content of German Patent Application 35 08 051.

As part of the teaching according to this invention, it is preferable to use the strongly pearlescing compounds of classes (A1) and (A2).

Such pearlescent concentrates whose pearlescing components consist of at least 70 wt%, in particular at least 90 wt% ethylene glycol distearate are especially preferred.

Examples of suitable emulsifiers (B) include nonionic, ampholytic and/or zwitterionic surfactant compounds which are characterized by a lipophilic group, preferably a linear alkyl or alkenyl group, and at least one hydrophilic group. This hydrophilic group may be either an ionic or a nonionic group.

Nonionic emulsifiers contain as the hydrophilic group, for example, a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups.

Especially preferred pearlescent concentrates include those which contain as emulsifiers the nonionic surfactants from the group of

(B1) addition products of 2 to 30 mol ethylene oxide and/or 0-5 mol propylene oxide onto linear fatty acids with 8 to 22 carbon atoms, onto fatty acids with 12 to 22 carbon atoms and on the alkyl phenols with 8 to 15 carbon atoms in the alkyl group,

(B2) C_{12}-C_{18} fatty acid mono- and diesters of the addition products of 1 to 30 mol ethylene oxide onto glycerol,

(B3) glycerol mono- and diesters and soribitan mono- and diesters of saturated and unsaturated C_8-C_{18} fatty acids and their ethylene oxide addition products,

(B4) C_8-C_{18} alkyl mono- and oligoglycocides and their exthoxylated analogs and

(B5) addition products of 10 to 60 mol ethylene oxide onto castor oil and hardened castor oil.

Also suitable are mixtures of compounds from several of these classes of substances.

The addition products of ethylene oxide and/or propylene oxide onto fatty alcohols, fatty acids, alkyl phenols, glycerol mono- and diesters and sorbitan mono- and diesters of fatty acids or onto castor oil or known products which are available commercially. These are homolog mixtures whose average degree of alkoxylation corresponds to the ratio of the quantities of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out.

C_{12}-C_{18} fatty acid mono- and diesters of the addition products of ethylene oxide onto glycine are known from German Patent 20 24 051 as moisturizing agents for cosmetic preparations. C_8-C_{18} alkyl mono- and oligoglycosides, their preparation and their use as surfactants are disclosed, for example, in U.S. Patent Application 3,839,318 A, U.S. Patent Application 3,707,535 A, U.S. Patent Application 3,547,828 A, German Patent Application 19 43 689 A, German Patent Application 20 36 472 A and German Patent Application 30 01 064 A as well as European Patent 77 167. They are synthesized in particular by reacting glucose or oligosaccharides with primary alcohols having 8 to 18 carbon atoms. With regard to the glycoside group, it is true that both monoglycosides in which a cyclic sugar group is bound with a glycosidic linkage to the fatty alcohol as well as oligomeric glycosides with a degree of oligomerization of up to preferably approximately 8 are suitable. The degree of oligomerization is a statistical average based on a homolog distribution which would be conventional for such technical grade products.

The compounds from group (B1) are especially preferred nonionic emulsifiers (B) as part of the teaching according to the present invention.

In addition, zwitterionic surfactants may also be used as emulsifiers (B). Zwitterionic surfactants are surface-active compounds which have at least one quaternary ammonium group and at least one -$COO^{(-)}$ group or -$SO_3^{(-)}$ group in the molecule. Especially suitable zwitterionic surfactants include the so-called betaines such as N-alkyl-N,N-dimethylammonium glycinates, e.g. coconut alkyl dimethylammonium glycinate, N-acyl-aminopropyl-N,N-dimethylammonium glycinates, e.g. coconut acylaminopropyl dimethylammonium glycinate and 2-alkyl-3-carboxylmethyl-3-hydroxyethyl-imidazolines each with 8 to 18 carbon atoms in the alkyl or acyl group as well as coconut acylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known by the CTFA designation cocamidopropyl betaine is especially preferred.

Other suitable emulsifiers (B) include ampholytic surfactants. The term "ampholytic surfactant" is understood to refer to surface-active compounds which also have at least one free amino group and at least one -COOH- or -SO_3H- group in the molecule in addition to C_8-C_{18} alkyl or acyl group and which are capable of forming internal salts. Examples of suitable ampholytic surfactants include N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyl taurines, N-alkyl sarcocines, 2-alkylaminopropionic acids and alkylamino acetic acids, each with approximately 8 to 18 carbon atoms in the alkyl group. Especially preferred ampholytic surfactants include N-cocoalkyl aminopropionate, cocoacyl aminoethyl aminopropionate and C_{12}-C_{18} acyl sarcosine.

As part of the teaching according to the present invention, the pearlescent concentrates may contain representatives of one or more of the above-mentioned classes of surfactants. When using mixtures, it is preferable to use nonionic and zwitterionic and/or ampholytic surfactants in a weight ratio of 5:1 to 1:5.

The pearlescent concentrates according to this invention which contain only nonionic, zwitterionic and/or ampholytic surfactants have proven to be universally applicable and to have an especially good tolerability with aqueous preparations of water-soluble surface-active substances of any type and ionicity.

If desired, the pearlescent concentrates may also contain anionic or cationic emulsifiers, however.

Such anionic emulsifiers include for example alkyl sulfates and alkyl polyethylene glycol ether sulfates with 1 to 6 ethylene glycol ether groups in the molecule which are used in the form of their alkali salts, magnesium salts, ammonium salts, mono-, di- or trialkanol ammonium salts with 2 to 3 carbon atoms in the alkanol group. Other suitable anionic surfactants include alkane sulfonates, α-olefin sulfonates, α-sulfo fatty acid methyl esters, fatty alcohol (polyglycol ether) carboxylates, sulfosuccinic acid, mono- and dialkyl esters, sulfosuccinic acid ester salts, acyl isoethionates, acyl taurides and acyl sarcocides. Soaps may also be used as emulsifiers. This may be achieved, for example, by saponifying a small portion, i.e., approximately 1 to 20 wt% of the linear saturated fatty acids by adding alkali hydroxide and in this way converting it to an anionic emulsifier. Preferred anionic surfactants include the alkyl polyethylene glycol ether sulfates such as sodium lauryl polyglycol ether sulfate.

Suitable cationic emulsifiers include quaternary ammonium surfactants such as alkyl trimethylammonium chlorides and dialkyldimethylammonium chlorides such as cetyl trimethylammonium chloride, stearyl trimethylammonium chloride, distearyldimethylammonium chloride, lauryl dimethylammonium chloride and lauryl dimethylbenzylammonium chloride, cetylpyridinium chloride and tallow alkyltris-(oligooxyalkyl) ammonium phospate.

The alkyl groups in the above-mentioned anionic and cationic surfactants usually contain 8 to 22 carbon atoms, especially 12 to 18 carbon atoms.

The compounds with alkyl groups which are used as surfactants here may be uniform substances. However, it is preferable to start with native animal and vegetable raw materials in the production of these substances, thus yielding substance mixtures with different alkyl chain lengths depending on the respective raw material used.

The deciding factor for the free-flowability or pumpability of the pearlescent concentrates according to this invention is the presence of low molecular polyhydric alcohols. Preferred low molecular polyhydric alcohols for this application contain 2 to 6 carbon atoms and 2 to 6 hydroxyl groups. Such alcohols include, for example, ethylene glycol, 1,2- and 1,3-propylene glycol, glycerol, di- and triethylene glycol, erythritol, arabitol, adonite (ribitol), xylitol, sorbitol, mannitol and dulcitol. It is especially preferable to use compounds that are liquid at room temperature, especially 1,2-propylene glycol and/or glycerol.

In the case of pearlescent concentrates containing less than approximately 30 wt% pearlescing components, it has proven sufficient in many cases if the low molecular polyhydric alcohol content amounts to about 1 wt%. This is true in particular when 1,2-propylene glycol and/or glycerol is used as the alcohol component.

In addition, the pearlescent concentrates according to this invention contain essentially water. Conventional commercial preservatives are added in subordinate amounts to preserve them and prevent bacterial and fungal infestations. In addition, buffer substances may also be added in subordinate amounts to adjust the pH to levels between 2 and 8, e.g., citric acid and/or sodium citrate.

The pearlescent concentrates according to this invention are pumpable in a temperature range of at least 5 to 40°C and remain stable in storage over long periods of time, i.e., at least about 3 months.

The pearlescent concentrates according to this invention are produced preferably by heating components (A), (B) and (C) first jointly to a temperature about 1 to 30°C above the melting point. In most cases, this will be a temperature of about 60 to 90°C. Then, water heated to approximately the same temperature is added to this mixture. If an ionic, water-soluble surfactant is used as the emulsifier, it may be preferable to dissolve the surfactant in the aqueous phase and add it to the mixture together with the water. The aqueous phase may also optionally contain the buffer substances in solution. The resulting dispersion is then cooled to room temperature i.e. about 25°C while stirring steadily. In most cases, the viscosity of the pearlescent concentrate will be so low that it is unnecessary to use special stirring equipment such as homogenizers or other high-speed mixing equipment. Temperature sensitive preservatives should not be added until after the mixture has been cooled to temperatures below 40°C, especially just before the end of the cooling process at temperatures of about 30°C.

The pearlescent concentrates according to this invention are suitable for producing opaque and pearlescent liquid aqueous preparations of water-soluble surface-active substances. They may be incorporated into liquid detergents and cleaning agents, for example, such as dishwashing products, liquid delicate detergents and liquid soaps, but preferably into liquid body cleaning and care products such as shampoos, liquid hand and body washes, shower preparations, bath additives (bubble baths), hair rinses or hair dyeing preparations.

To produce the pearlescence, the pearlescent concentrates according to this invention are added in an amount of 1 to 10 wt%, especially 1.5 to 5 wt% to the clear aqueous preparations at 0 to 40°C and distributed therein by stirring. Depending on the preparation and the use concentrate, this yields a highly to weakly shiny, extremely dense pearlescence with a metallic sheen.

The following examples are presented to explain the object of this invention in greater detail without limiting it in any way.

Examples

Free-flowing pearlescent concentrates with the compositions listed in Table 1 were prepared. When using dilute solutions of components (A) and (B), the amounts given are based on weight percent active substance. In the case of the substances listed with their commercial brand names, these are listed below:

1. Ethylene glycol distearate (at least 90% diester) (Henkel)
2. Coco fatty acid monoethanol amide (approximately 95% amide) (Henkel)
   Composition of the fatty acid:
   approx. 56% lauric acid
   approx. 21% myristic acid
   approx. 10% palmitic acid
   approx. 13% stearic acid and oleic acid
3. C_{12}-C_{14} fatty alcohol + 4 ethylene oxide units (Henkel)
4. Aqueous solution of a fatty acid amide derivative with a betaine structure of the formula $R\text{-}CONH\text{-}(CH_2)_3\text{-}N^+(CH_3)_2\text{-}CH_2\text{-}COO^-$ with the CTFA designation cocamidopropyl betaine (approx. 30% active substance, approx. 5% NaCl) (Henkel)
5. C_{12}-C_{14} fatty alcohol + 3 ethylene oxide units (Henkel)
6. 86% in water

Table 1: Free-flowing pearlescent concentrate

	Content (wt%) Mixture No.											
Components	1	2	3	4	5	6	7	8	9	10	11	12
Pearlescing substance (A)	25	25	25	30	30	30	25	25	25	25	25	25
including:												
Cutina® AGS [1]	25	25	25	30	30	25	25	25	25	25	25	25
Comperlan® 100[2]	-	-	-	-	-	5	-	-	-	-	-	-
Emulsifier (B)	19	17	19	20.5	20.5	20.5	17	18	17	17	19	18.5
including:												
Dehydol® LS4 [3]	5	11	5	13	13	13	11	8	11	11	5	11
Dehyton® K [4]	9	6	9	7.5	7.5	7.5	6	6	6	6	9	7.5
Dehydol® LS3 [5]	5	-	5	-	-	-	-	4	-	-	5	-
Alcohol (C)	1	5	1	5	5	5	5	1	1	1	1	5
including:												
Glycine [6]	-	5	1	5	-	5	-	-	1	-	1	3
1,2-propylene glycol	1	-	-	-	5	-	5	1	-	1	-	2
Water Preservative Suspension agent	<---------- to a total of 100 ---------->											

The amounts of components A, B and C used were heated to a temperature of 75°C. Then the water added to 75°C was added to this melt. While stirring constantly, the dispersion was then cooled to 25°C, whereupon the preservative was added at a temperature of 30°C.

The viscosities of the pearlescent concentrates were determined with a Brookfield RVF viscometer, spindle 5, 10 rpm, always at the temperature at which the mixture had been stored. The comparative mixture Vx had the same composition as mixture x except for the missing component C. The measured values are summarized in Table 2.

Table 2: Viscosity values

Mixture No.	Temperature (°C)	Storage Time (days)	Viscosity (mPas)
2	10	1	14400
2	25	1	6000
2	40	1	14000
7	19	1	14000
7	25	1	5600
7	40	1	8000
9	10	14	14000
V9	10	14	22000
9	25	1	6000
V9	25	1	11200
9	25	7	5200
V9	25	7	12000
9	25	14	5200
V9	25	14	12000
9	40	14	14000
V9	40	14	20000
10	10	14	16000
V10	10	14	22000
10	25	1	6000
V10	25	1	11200
10	25	7	6000
V10	25	7	12000
10	25	14	6400
V10	25	14	12000
10	40	14	13600
V10	40	14	20000

These results show the definite reduction in viscosity due to the addition of the alcohol.

Application examples

1) Shampoo with anionic surfactants

Component	Wt%
Fatty alcohol (C_{12}-C_{14}) polyglycol (2 EO) ether sulfate, sodium salt, approx. 30% in water (CTFA designation: sodium laureth sulfate)	40.0
N-cocoacylamidopropyl dimethylglycine, 30% in water (CTFA designation: cocamidopropyl betaine)	10.0
Cetiol® HE [7]	2.0
Pearlescent concentrate mixture 9	3.0
Sodium chloride	0.8
Water	to a total of 100

2) Bubble bath with anionic surfactants

Component	Wt%
Fatty alcohol (C_{12}-C_{14})-sulfate, magnesium salt, approx. 30% in water (CTFA designation: magnesium lauryl sulfate)	40.0
N-cocoacylamidopropyl dimethylglycine, 30% in water (CTFA designation: cocamidopropyl betaine)	10.0
Sulfosuccinic acid monolauryl polyglycol (3 EO) ester, 40% in water (CTFA designation: disodium laureth sulfosuccinate)	4.5
Cetiol® HE [7]	2.0
Pearlescent concentrate mixture 7	3.0
Sodium chloride	0.3
Water	to a total of 100

3) Hair treatment product with cationic surfactants

Component	Wt%
Quaternum-52 [8]	2.0
Cetiol® HE	0.5
Viscontran® HEC 30000 PR [9]	50.0
Pearlescent concentrate mixture 2	5.0
Citric acid	0.2
Water	to a total of 100

[7] Polyol fatty acid ester (CTFA designation: PEG-7-glyceryl cocoate) (Henkel)

[8] Tris-(oligooxyethyl)-alkylammonium phosphate, 50% in water (Henkel)

[9] Hydroxyethylcellulose, 2% in water (Aqualon)

[Claims are in English]